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PREPARATION OF CdS SINGLE CRYSTALS AND THEIR STRUCTURAL AND ELECTROPHYSICAL PROPERTIES

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ABSTRACT

Description of a procedure for growing granular CdS single crystals by the zone sublimation method. An X-Ray analysis of structural defects demonstrates the superiority of the crystals over those obtained by the recrystallization method. The photosensitivity curves obtained for the crystals exhibit a broad maximum. The depth of levels and the concentration of capture levels are determined.

The article (Ref. 1) has described a method for preparing CdS /171* single crystals, as well as their structural and certain physical properties. It has been determined that single crystals, obtained by the recrystallization method, show extreme destruction of the lattice, and a large dislocation density ($\sim 10^6$ cm^{-2}). At the same time, their electrophysical properties were a little better, in the sense of the

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* Note: Numbers in the margin indicate pagination in the original foreign text.

capacity to receive special radiation, than the properties of single CdS crystals obtained by other methods.

Progress in the scientific study of semiconductors requires preparation of crystals with different admixture concentration, dislocation density, and different degree of perfection of the crystal lattice. The results of an investigation, concerned with large single CdS crystals obtained by the method of zone sublimation, are given below.

Method of Preparing Large Single Crystals of A_2B_6 Compounds

In order to obtain large crystals of various compounds of the type A_2B_6, we have used the method of zone sublimation. A necessary condition for growing crystals by this method is a relative displacement of the container with the working substance with respect to the electric furnace. We have chosen a version involving a movable electric furnace and a fixed container. The furnace was moved by means of an electric control KEP-12u which enabled the authors to change the speed according to a given program. Figure 1 shows the position of the container 3 (quartz tube) in the electric furnace 1, and the temperature distribution. The speed with which the furnace was displaced was 0.5 - 1 mm/hour. The temperature of the furnace was controlled during the whole growing cycle by means of a platinum-platinum-rhodium thermocouple. The use of a powerful electronic stabilizer enabled us to keep the temperature conditions constant during the entire growing cycle ($\sim$ 100 hours) with an accuracy of $\pm$ 5°C. CdS and CdSe crystals were grown from luminophorous

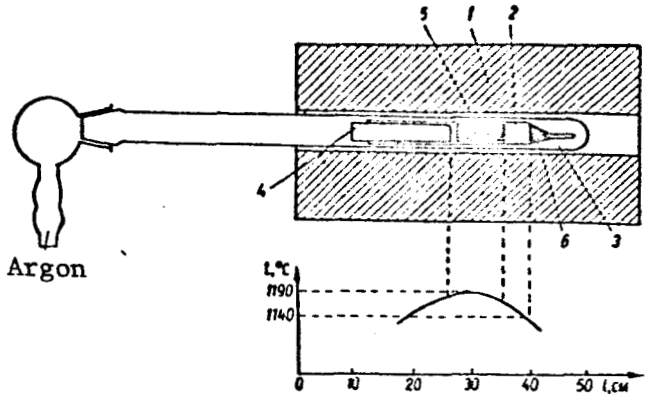

Figure 1

Diagram of the Experimental Apparatus for Growing Large Single CdS Crystals

1 - Movable electric furnace; 2 - Vial; 3 - Quartz container; 4 - Muffler; 5 - Working substance (CdS); 6 - CdS single crystal.

powder which had been previously treated by various methods. The starting of the apparatus and the operational regime were analogous to those described in (Ref. 2). The initial runs were conducted in an atmosphere of nitrogen; argon, however, turned out to be more favorable.

Figure 2a shows the single CdS and CdSe crystals obtained by the authors. From such single crystals, samples were prepared for studying their structural peculiarities and the Hall effect; the orientation relative to the crystallographic planes was taken into account. Figure 2b shows a single crystal with a natural face ("freely grown"). Such single crystals were obtained by means of the described apparatus, but without displacing the furnace with respect to the container.

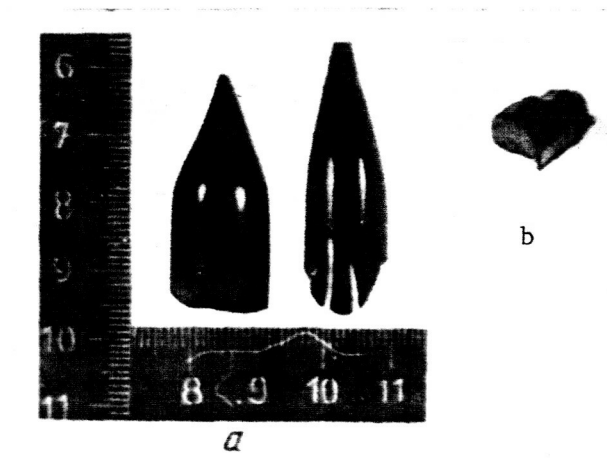

Figure 2

a - Single CdS and CdSe Crystals; b - "Freely Grown" Single CdS Crystal (Scale 1:1)

Investigation of Defects in the Crystal Structure /172

A great number of studies have been made on thin single CdS crystals obtained by the method of Frerichs (Ref. 3). Their structural imperfections have been sufficiently explored by various authors using the method of selective etching (Ref. 4), X-Ray diffraction microscopy (Ref. 5, 6), transmission electron and microscopic methods (Ref. 7). These studies have shown that the obtained crystals contain dislocations, whose concentration was different for different samples (10^2 - 10^3 cm^{-2}), packing defects, defects resulting from the segregation of the admixtures, and also defects due to deviations from stoichiometry.

We performed X-Ray studies of both "zonal" and "freely grown" single crystals of a prismatic form with a natural face. In order to reveal

Figure 3

Etching Figures on a Plane (0001) in CdS (Etching in a Solution of 60 g $CdCl_2$ + 100 ml Hcl during 20 sec), x 600

structural defects, the effect of the anomalous passage of X-Rays through the crystals (Ref. 8) and the etching method were investigated. The /173 samples were ground in the direction parallel to the cleavage plane, which coincides with the crystallographic planes $(11\bar{2}0)$ or $(10\bar{1}0)$, their thickness being 150-200 microns.

In a boiling etching agent (1 part by weight of KJ + 1 part by weight of $C_6H_8O_7 \cdot H_2O$) the samples were etched, reaching thicknesses which corresponded to the value $\mu_0 t = 5 - 8$, where μ_0 is the linear index of refraction of X-Rays, and t is the thickness of a crystal. The work was conducted using X-Ray equipment URS-501 (radioactive CuK_α).

As the monochromator, a germanium single crystal was used, which was cut in the direction parallel to the crystallographic plane (111). In the case of single crystals with large thicknesses, a continuous

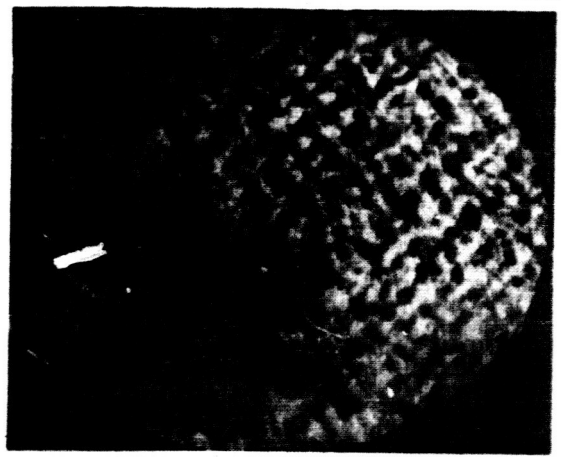

Figure 4

Microroentgenogram of CdS.
Diffraction plane (0001). x32.

radiation was also used.

The general scheme of the experiment is similar to that described in (Ref. 8). All crystals studied by us had a lattice of the zinc sulfide type.

The dislocation thickness for various samples of single crystals, obtained by the zone sublimation method, was 10^4 - 10^5 cm^{-2}.

The dislocation density for "freely grown" single crystals was a little smaller (for certain samples only 10^2 - 10^3 cm^{-2}). On the microphotographs (Figure 3), in addition to etching cavities with vortices, one can see plane-bottom cavities which are characteristic of the accumulation of admixture atoms, or of excess atoms or vacancies.

The half-width of the oscillation curves, measured by means of a double-crystal spectrometer, was 30". For a considerable fraction of

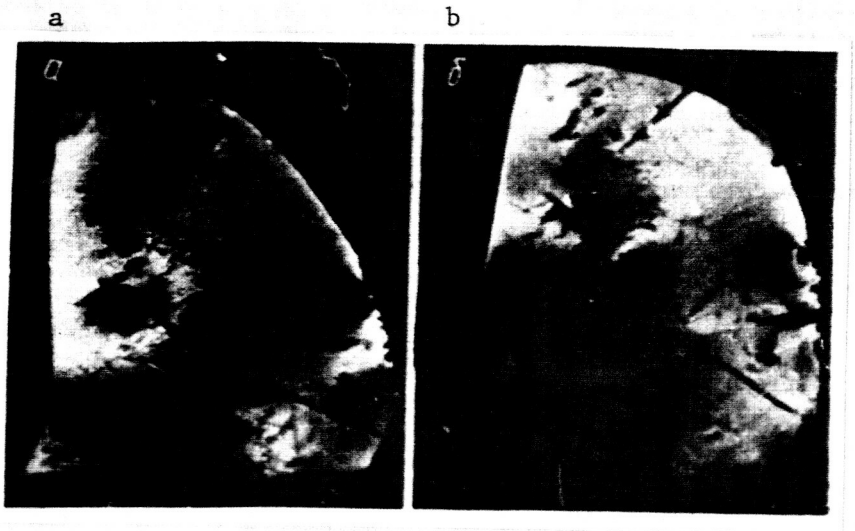

Figure 5

Microroentgenogram of a "Freely Grown" CdS Single Crystal, x32.
a - Diffraction Plane $(11\overline{2}0)$; b - Diffraction Plane $(10\overline{1}0)$.

these crystals, during the investigation of the anomalies in the transmission of light, the obtained reflexes R (the diffracted beam) were more intense than T (transmitted beam). This indicates the presence of microstresses in the crystals which, certainly, are the result of the growing process.

For a great number of crystals of both types, their microroentgenogram shows a characteristic cell structure (Figure 4) which veils the picture of the dislocation distribution.

Consecutive washing etching of a crystal to an approximate depth of 20 microns did not lead to a change in the character of the obtained diffraction pattern.

The cell character of the structure is characteristic of specially

alloyed Ga and In crystals in the growing process, as well as the un- /174
alloyed crystals, but with changed stoichiometry and oxygen admixtures.

This circumstance, and slso the fact that the picture contrast on the microphotographs does not change when the reflection plane is varied, allow us to draw the following conclusion. The lattice defects, which we see on the microphotographs, are most likely related to the segregation of the excess atoms (with respect to stoichiometry), or of other admixtures, which create local stresses in the region. These facts influence the intensity of the diffracted X-Ray beam.

Among the ten crystals, which were studied by the authors, we discovered one of a number of "freely grown" crystals which was devoid of the characteristic trait of the others -- namely, the cell structure. In this crystal we discovered defects which are normal for CdS crystals: dislocations, concentrations of admixtures (Figure 5, a and b), which are observed in CdS crystals obtained by other methods (Ref. 5).

Certain Electrophysical Properties of CdS Single Crystals /175

In order to investigate the electrophysical properties of CdS crystals, samples were cut off from a large single crystal in the direction parallel to the C axis, and ground to the form of parallel-pipeds of dimensions $4 \times 3 \times 1$ mm^3, with the largest dimension along the direction of the hexagonal axis. The treatment of the crystal surfaces was conducted in the same way as for X-Ray structural analyses.

The authors studied a number of electrophysical characteristics of single crystals with deposited indium contacts.

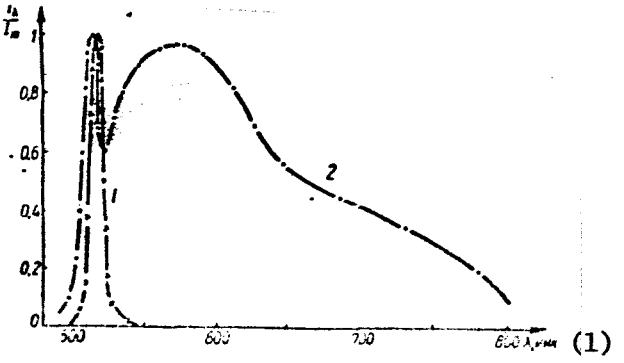

Figure 6

Spectral Distribution of Photosensitivity
(1)- millimicron

Dark resistance. During the measurement of a specific resistance, a constant voltage of several to 40 volts was applied to the sample. The samples were kept in darkness at room temperature for 20 - 24 hours. The dark resistances of the samples, prepared from different single crystals, differed by several orders of magnitude, and those of the samples prepared from the same single crystal differed by several times. The specific resistance of the samples prepared from different single crystals varied from $7 \cdot 10^9$ to 10^{13} ohm-cm.

Photosensitivity. The photosensitivity of the samples was measured at a constant applied voltage of 12.5 volts, and the illumination was 200 lux.

As in the previous case, the photosensitivities of the samples prepared from one single crystal differed slightly, whereas those of the samples prepared from different single crystals differed by several orders of magnitude. The photosensitivity of better samples amounted to

$2 \cdot 10^{-6}$ a/volt-lux.

Spectral distribution of photosensitivity. Based on the spectral distribution of the photosensitivity (Figure 6, curves 1 and 2 shown for different energies), we can draw the conclusion that the investigated CdS single crystals differ strongly in their purities. The main maximum of the photoconductivity of CdS single crystals is located in the 514-520 millimicrons range. In the case of single crystals with a large concentration of admixtures, in addition to the principal maximum, there is a broad admixture maximum in the 560 - 570 millimicrons region (Figure 6, curve 2). The red boundary of the admixture photoconductivity is 850 millimicrons.

Thermostimulated conductivity. The curves of the thermostimulated conductivity have a similar appearance for CdS (Ref. 9, 10) and enable us to find the depth of the region of the capture levels. Calculations showed the presence of capture levels at the depth of 0.13 - 0.16 eV and 0.42 - 0.46 eV for conductivity zones. The concentration of the capture levels calculated from the area under the curve of the thermostimulated conductivity (taking into consideration the temperature dependence of the lifetime τ and of the electron mobility) amounted to $8 \cdot 10^{13}$ - $3 \cdot 10^{15} cm^{-3}$.

Conclusions /176

One characteristic trait of CdS single crystals, grown by the zone sublimation method, is the presence of a region of disruptions which may represent the aggregate of excess or admixture atoms.

The half-width of the oscillation curves, the relatively large

dislocation density, and also the presence of large disruption regions foster the conclusion that these crystals are not perfect enough, as far as their structure is concerned. However, the single crystals studied by the authors have better structural traits and electrophysical properties than those described in (Ref. 1).

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Institute of Physics of the
Ukrainian SSR Academy of Sciences, Kiev

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